

REVERSIBLE BINDING OF HUMIC SUBSTANCES TO CLAY COLLOIDS

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INTRODUCTION

The aqueous transport of organic pollutants and toxic metal ions in the surface and subsurface environment is strongly influenced by adsorption reactions with sediments and/or suspended colloids. Organic coatings are very common on such particles and their presence greatly alters the adsorption process (Hunter, 1980; Ballistrieri et al., 1981; Davis, 1982). Another reason for interest in organic-clay complexes is their recently discovered usefulness in removing compounds such as chloroanilines from wastewaters (Boyd and Mortland, 1986; Mortland et al., 1986; Warren et al., 1987). To date, efforts to quantify this adsorption process have not adequately dealt with the fact that dissolved organic matter (DOM) is a complex heterogeneous mixture. DOM in surface and ground waters consists of an extremely large number of compounds, each with its own set of physical and chemical properties (Perdue, 1985). Under appropriate conditions (pH, ionic strength, DOM concentration, etc.), some components of DOM associate with inorganic matter (clays, metal oxides, etc.) to form organically coated colloids. Understanding these conditions is crucial in modeling binary and ternary transport systems involving DOM, inorganic colloids, and pollutants. Variations in the properties of adsorbed DOM partitioned onto colloids will ultimately be manifested in corresponding variations in the affinity of the colloidal particles for water-borne contaminants.

In this study, new techniques are being used to detect changes in the composition of dissolved and adsorbed organic matter during the fractionation of DOM by selective adsorption onto colloidal surfaces. These methods are expected to reveal, under a given set of conditions, which organic functional groups have a preference for adsorption to a given colloid and quantitative

information on the energetics of the adsorption process. This is a report of the work currently in progress.

PROTOCOL AND PROCEDURE

There are many variables to consider when modeling clay-organic interactions in the environment, e.g., clay type, composition of the organic matter, ratio of clay to organic matter, inorganic ions present, ionic strength, and pH. Due to the inherent time and resource constraints of this study, only a few of these variables are being examined. A single clay (Ca-montmorillonite) and only one source of organic matter (Suwannee River near Fargo, GA) are used. In this study, DOM adsorption and fractionation is observed at several clay-organic mixing ratios at several pH's (5, 7 and 9) and ionic strengths (0.01 and 0.1).

The experiments are discontinuous titrations consisting of five points with DOM:clay ratios of 0.01, 0.1, 1, 10, and 100. Experiments are conducted for each of the 12 combinations of pH, ionic strength, and DOM (10 and 100 mg/l). After equilibration at 298K, the aqueous and particulate phases are separated by high-speed centrifugation. A portion of the clay fraction is retained for inspection by SEM to determine the morphology of the clay-organic complexes. The remaining adsorbed organic matter is extracted by addition of NaOH for subsequent analysis.

The isolated organic matter from both phases is subjected to elemental analysis and analysis of major oxygen-containing functional groups. Total acidity is determined by back-titration of an ultrafiltered solution of DOM in 0.1 N Ba(OH)₂ (see Perdue, 1985). The resolution of total acidity into stronger and weaker classes of acidic functional groups (e.g., carboxylic acids and phenols) is operationally achieved by fitting direct potentiometric titra-

tion data to the Gaussian distribution model of proton binding sites (Perdue et al., 1984). The abundances of other oxygen-containing functional groups are determined by measuring changes in elemental composition that result from formation of specific derivatives: carbonyl groups by oximation, hydroxyl groups by acetylation, and carboxyl groups by amidation. This combination of classical functional group derivatization techniques with elemental analyses was recently used successfully by Portal et al. (1986) and Pillon et al. (1986) to characterize humic acids from soils and deltaic sediments.

The elemental and functional group analyses can be used to estimate levels of aliphatic and aromatic carbon in the adsorbed and non-adsorbed fractions of DOM (Perdue, 1984). These numerical estimates are usually in excellent agreement with NMR estimates of carbon distribution in humic substances (Wilson et al., 1987). The results from all physical and chemical characterizations will be integrated to describe changes in the chemical properties of DOM and adsorbed organic matter as the extent of binding of DOM varies from zero to the highest achievable levels.

EXPECTED RESULTS AND BENEFITS

We anticipate that our research will lead to a conceptual model for understanding how the binding of contaminants to organically coated colloids varies with the extent of DOM binding to the colloidal particles. In particular, data for the fractionation of DOM on Camontmorillonite at various pH's and ionic strengths will be generated. It is anticipated that the DOM that can be adsorbed at very high DOM-clay ratios will have a much higher affinity for the clay than bulk DOM and will differ physically and chemically from bulk DOM. These differences will gradually diminish as a larger fraction of DOM is adsorbed at low DOM-clay ratios.

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